

PAT-NO: JP410158224A
DOCUMENT-IDENTIFIER: JP 10158224 A
TITLE: PRODUCTION OF UNSATURATED QUATERNARY AMMONIUM SALT
PUBN-DATE: June 16, 1998

INVENTOR- INFORMATION:

NAME
KIKUCHI, KATSUAKI
NAKAHAMA, TETSURO
SATO, FUMIO

ASSIGNEE- INFORMATION:

NAME	COUNTRY
NITTO CHEM IND CO LTD	N/A
NITTO RIKEN KOGYO KK	N/A

APPL-NO: JP08330191

APPL-DATE: November 27, 1996

INT-CL (IPC): C07C219/08, C07C213/02, C07C213/10

ABSTRACT:

PROBLEM TO BE SOLVED: To produce an unsaturated quaternary ammonium salt of quality crystals that is a monomer used as a material for production of cationic polymers used for flocculating agents and antistatic agents by the use of a solvent of high stability to organisms.

SOLUTION: This unsaturated quaternary ammonium salt of quality crystals is obtained by making an unsaturated tertiary amine of formula I ($R<SB>_1</SB>$ is H, $CH<SB>_3</SB>$; $R<SB>_2</SB>$ and $R<SB>_3</SB>$ are each $CH<SB>_3</SB>$ or $C<SB>_2</SB>H<SB>_5</SB>$), for example, dimethylaminoethyl methacrylate, with an alkyl halide, for example, methyl chloride, in a quantity of the same

molar number as that of the unsaturated tertiary amine in acetone or N-methylpyrrolidone at temperature of 0-60°C for 5-8hr, and filtering out the crystal precipitation after the completion of the reaction, washing the crystals lightly with a solvent, for example, acetone, which does not so dissolve the crystals but dissolves well the solvent used for the reaction, and then evaporating off the solvents and other evaporative substances, by heating or vacuum drying.

COPYRIGHT: (C)1998,JPO

Disclaimer:

This English translation is produced by machine translation and may contain errors. The JPO, the INPI, and those who drafted this document in the original language are not responsible for the result of the translation.

Notes:

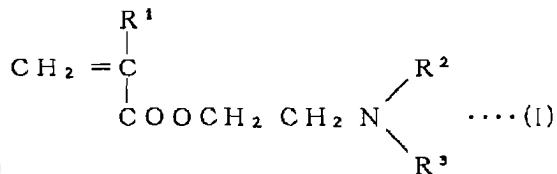
1. Untranslatable words are replaced with asterisks (****).
2. Texts in the figures are not translated and shown as it is.

Translated: 20:42:21 JST 08/10/2009

Dictionary: Last updated 07/09/2009 / Priority: 1. Chemistry / 2. Medical/Pharmaceutical sciences / 3. Biotechnology

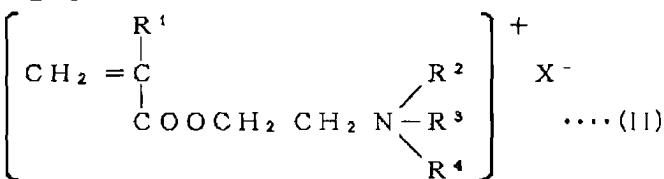
CLAIM + DETAILED DESCRIPTION

[Claim(s)]



[Claim 1]Formula (I)

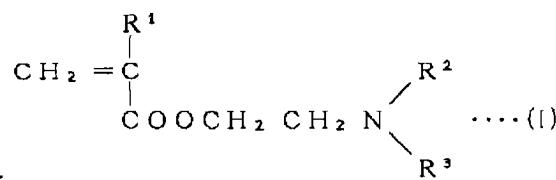
Unsaturated tertiary amine and alkyl halide R^4X which are expressed with (however, R^1 shows $-\text{CH}_3$ or $-\text{C}_2\text{H}_5$, as for $-\text{H}$ or $-\text{CH}_3$, R^2 , and R^3). It makes it react (however, R^4 shows $-\text{CH}_3$ or $-\text{C}_2\text{H}_5$, and X shows Cl , Br , or I), 4 class is formed, and it is formula (II).



A manufacturing method of a good-quality crystal of said unsaturated quarternary ammonium salt which is characterized by making this reaction perform in acetone or N-methylpyrrolidone in manufacturing unsaturated quarternary ammonium salt expressed with (however, R^1 , R^2 , R^3 , R^4 , and X are the same as a front).

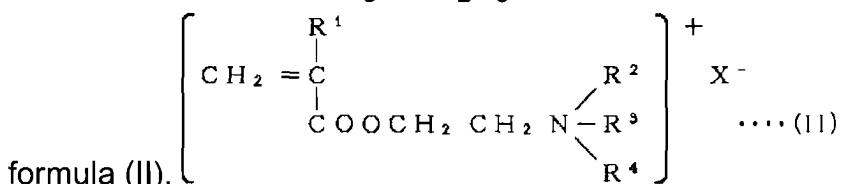
[Detailed Description of the Invention]

[0001]



[Field of the Invention] This invention is formula (I).

Unsaturated tertiary amine (I) expressed with (however, R^1 shows $-\text{CH}_3$ or $-\text{C}_2\text{H}_5$, as for $-\text{H}$ or $-\text{CH}_3$, R^2 , and R^3) under existence of a specific solvent The alkyl halide R^4X . It makes it react (however, R^4 shows $-\text{CH}_3$ or $-\text{C}_2\text{H}_5$, and X shows Cl , Br , or I), 4 class is formed, and it is



formula (II).

The good-quality crystal of unsaturated quarternary-ammonium-salt (II) expressed with (however, R^1 in formula, R^2 , R^3 , R^4 , and X are the same as a front) is related with a high grade and the method of manufacturing advantageously industrially. The unsaturated quarternary ammonium salt obtained by this invention is a useful monomer used as the manufacturing raw materials of cationic polymer used for a flocculant, an antistatic agent, a soil conditioner, an electric conduction processing agent, a dyeing improving agent, a paper reinforcing agent, the filtration improvement agent of paper, cosmetics, etc.

[0002]

[Description of the Prior Art] The reaction which forms tertiary amine into 4 class by the 4th class-sized agent, and manufactures quarternary ammonium salt is made carrying out under existence of a polar high solvent, for example, water, an alcohol, etc. conventionally has a quick reaction, and advantageous [a thing]. When [however,] alkyl halide R^4X is made to react to said unsaturated tertiary amine (I) under existence of water, an alcohol, etc., Since generated unsaturated quarternary-ammonium-salt (II) is dissolving into a solvent, distillation or other means must remove a solvent to dissociate as a crystal, and time and effort is hard for it. Moreover, it is difficult to remove an unreacted raw material, i.e., unsaturated tertiary amine (I), and alkyl halide R^4X only by removing a solvent. For this reason, in order to lessen an unreacted raw material as much as possible, it is performing a reaction under pressurization in many cases, and raising conversion is reported, but this also needs high pressure gas equipment and the reaction of unsaturated tertiary amine (I) and alkyl halide R^4X poses a problem of equipment. Since solvents, such as water and an alcohol, have high reactivity, solvolysis of a part of unsaturated tertiary amine (I) is carried out, but it is also difficult to

remove this decomposition product. Thus, it is difficult to obtain the unsaturated-quaternary-ammonium-salt (II) crystal of a high grade by using water, an alcohol, etc. as a solvent.

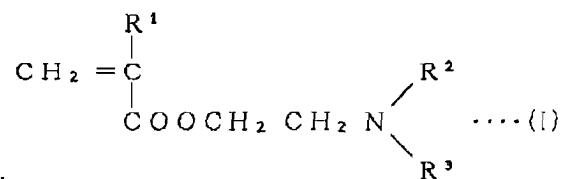
[0003] Since unsaturated quarternary-ammonium-salt (II) does not melt into a nonpolar solvent, for example, hydrocarbons, easily, on the other hand, Since the crystal of unsaturated quarternary-ammonium-salt (II) deposits only by making it react when alkyl halide R^4X is made to react to unsaturated tertiary amine (I) under these existence, do not need distillation after a reaction but it is advantageous operationally, but. It is hard to deal with it by mucus, filtration and other operations with a solvent contain impurities, such as not being not only easy but an unreacted material, and a solvent, during the crystal, and the good thing cannot say the obtained crystal. Although obtaining a good-quality crystal as a solvent is reported in acetonitrile by JP,56-49897,B, acetonitrile is a work top problem in the Patent Law Section 2 deleterious substance of poison and the deleterious substance controlling method. Although the manufacturing method which uses acetone as a solvent by JP,60-54343,A or JP,61-50947,A is reported, it is a mixed solvent with water, and since acetone is eventually distilled off and an aqueous solution is obtained, neither a hydrolysis product nor an unreacted raw material can be removed. Although the manufacturing method which uses acetone as an independent solvent by JP,59-110660,A is reported, This method adds water after a reaction, since it has obtained the unsaturated quarternary-ammonium-salt aqueous solution by separating a water layer, cannot remove a water-soluble impurity in which tertiary amine carried out solvolysis, and cannot obtain a high grade crystal.

[0004]

[Problem to be solved by the invention] This invention was made that the fault of this conventional technology should be improved, and Unsaturated tertiary amine (I), In making alkyl halide R^4X react under existence of a solvent, and obtaining the crystal of unsaturated quarternary-ammonium-salt (II), let the method of manufacturing the good-quality crystal of unsaturated quarternary-ammonium-salt (II) with high yield using the solvent with high safety to an organism be a technical problem.

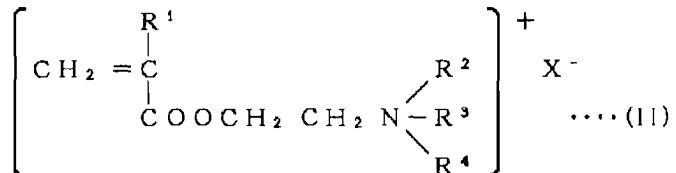
[0005]

[Means for solving problem] As a result of inquiring wholeheartedly that said technical problem should be solved, when acetone or N-methylpyrrolidone was used as a solvent, this invention persons found out depositing the good-quality crystal of unsaturated quarternary-ammonium-salt (II) with high yield, and reached this invention.



[0006] That is, this invention is formula (I).

Unsaturated tertiary amine (I) and alkyl halide R^4X which are expressed with (however, R^1 shows $-CH_3$ or $-C_2H_5$, as for $-H$ or $-CH_3$, R^2 , and R^3). It makes it react in acetone or N -methylpyrrolidone (however, R^4 shows $-CH_3$ or $-C_2H_5$, and X shows Cl, Br, or I), 4 class is



formed, and it is formula (II).

It is the method of manufacturing the good-quality crystal of the unsaturated quarternary ammonium salt expressed with (however, R^1 , R^2 , R^3 , R^4 , and X are the same as a front) with high yield.

[0007]As unsaturated tertiary amine (I) used for this invention, dimethylaminoethyl methacrylate, diethylamino ethyl methacrylate, dimethylamino ethyl acrylate, diethylamino ethyl acrylate, etc. are mentioned.

[0008]Ethyl halide like methyl halide like methyl chloride, a methyl bromide, and a methyl iodide, ethyl chloride, ethyl bromide, and ethyl iodide as alkyl halide, etc. are raised.

[0009] In operation of this invention, [as a reaction rate of unsaturated tertiary amine (I) and alkyl halide R^4X] It is preferred to use equimolar or alkyl halide superfluously, and 1-2 mol of alkyl halide usually uses 1-1.5 mol preferably to 1 mol of unsaturated tertiary amine (I)s.

[0010]Although the amount in particular of the solvent used is not specified, it is preferred to usually use 50-2000 ml to 1 mol of unsaturated tertiary amine (I)s, in view of the point of handling of a reaction mixture, and especially 200-1000 ml is preferred.

[0011]Although a reaction advances also at a room temperature, it is preferred to perform a rate of reaction at temperature beyond a room temperature from a point made quick, reaction temperature is 0-60 **, and 20-60 ** is usually especially suitable for it.

[0012]Since the boiling point is low, alkyl halide R^4X is good to usually teach unsaturated tertiary amine (I), a solvent, and a small amount of polymerization inhibitor to a proper reactor as a reaction method, to evaporate alkyl halide R^4X and to blow in a small quantity every into it.

[0013]Polymerization inhibitor is to prevent a monomer component (raw material amine and generated quarternary ammonium salt) from polymerizing during a reaction, and usually uses a proper quantity of hydroquinone, hydroquinone monomethyl ether, cupferron, phenothiazins, etc.

[0014]Although reaction time changes according to reaction temperature, an adding speed of alkyl halide R^4X , etc., it is usually 0.5 to 8 hours.

[0015]The system of reaction is suitably riped after an end of addition of alkyl halide R^4X if needed, and since a reaction is completed, a precipitated crystal is filtered. Subsequently, although solubility of a crystal [like acetone] whose obtained crystal is is low, after a solvent which dissolves well washes an impurity and a solvent lightly, they isolate as a good-quality crystal of a high grade by removing a residual solvent and other volatile matters by heating or reduced pressure drying.

[0016]

[Working example]Next, this invention is not restrained by the following embodiments although an embodiment explains this invention.

[0017]157 g (1 mol) of dimethylaminoethyl methacrylate, 375 ml of acetone, and the hydroquinone monomethyl ether 3.1g were taught to the 1000-ml reactor which embodiment 1 reflux condenser, the agitator, the thermometer, and the gas entrainment pipe were formed, and intercepted humidity. Subsequently, heating a reactor at 40 ** from the exterior, and agitating the liquid phase violently, 65 g (1.3 mol) of methyl chloride was blown, and was made to react over 6 hours. The amount of deposits of a crystal increases with advance of a reaction. After the end of an entrainment of methyl chloride, after cooling the reactant to the room temperature, the precipitated crystal was filtered and washed. Subsequently, the filtration crystal was dried at the temperature of 60 **, and a residual solvent and other volatile matters were removed. It was easy to deal with the obtained crystal by colorless needlelike non-mucus, it was checked as a result of analysis by an infrared absorption spectrum that they are $CH_2=C(CH_3) COO(CH_2)_2 N(CH_3)_3$ and Cl, and the yield was 92.4% (yield of 192g).

[0018]143 g (1 mol) of dimethylamino ethyl acrylate, 375 ml of acetone, and the hydroquinone monomethyl ether 3.1g were taught to the reactor same with having used in embodiment 2 Embodiment 1. Hereafter, the crystal of unsaturated quarternary ammonium salt was manufactured in accordance with the same method as Embodiment 1. As a result, the same good crystal as the case of Embodiment 1 was obtained. It was checked as a result of analysis by an infrared absorption spectrum that they are $CH_2=CHCOO(CH_2)_2 N(CH_3)_3$ and Cl, and the yield was 90.2% (yield of 174.7g).

[0019]157 g (1 mol) of dimethylaminoethyl methacrylate, 375 ml of N-methylpyrrolidone, and the hydroquinone monomethyl ether 3.1g were taught to the reactor same with having used in embodiment 3 Embodiment 1. Hereafter, the crystal of unsaturated quarternary ammonium salt was manufactured in accordance with the same method as Embodiment 1. As a result, the same good crystal as the case of Embodiment 1 was obtained. It was checked that they are $CH_2=C(CH_3) COO(CH_2)_2 N(CH_3)_3$ and Cl as a result of analysis by an infrared absorption spectrum, and the yield was 92.8% (yield of 193g).

[0020]

[Effect of the Invention]. Make acetone or N-methylpyrrolidone alkyl halide R^4X react to the above-mentioned unsaturated tertiary amine (I) as a solvent in this invention. Although both solvents are inertness and both raw materials often melt them in the reaction of unsaturated tertiary amine (I) and alkyl halide R^4X , unsaturated quarternary-ammonium-salt (II) which is an objective product is hardly melted. When [therefore,] alkyl halide R^4X is made to react to unsaturated tertiary amine (I) under existence of acetone or N-methyl pyrrolidone solvent, A reaction is not checked with a solvent and it was easy to deal with a precipitated crystal by non-mucus nature for that the crystal of unsaturated quarternary-ammonium-salt (II) deposits, and a desirable thing, and excluding an unreacted material, a solvent, etc., it is a high grade and it was found out that a yield is also high enough. And since a solvolysis product is also melted well, unsaturated quarternary-ammonium-salt (II) of a high grade can be obtained only by filtering the precipitated crystal. Even if it is a case where an unreacted raw material remains similarly, since dissociating is easy, a high grade crystal is obtained. For this reason, reacting by ordinary pressure also becomes it is possible and unnecessary [equipment of the pressurization reaction for raising conversion]. A solvent is removable only by elimination of the solvent which remains in addition being easy for unsaturated quarternary-ammonium-salt (II) which filtered the acetone solvent away after the reaction for volatility since the boiling point was low (56 ** of boiling points), when an acetone solvent is used, for example, heating a crystal.

[Translation done.]